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## (54) THIN FILM MAGNET AND ITS MANUFACTURE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide high magnetic characteristics at a low cost, by forming a hard magnetic phase and a soft magnetic phase, which mutually adjoin in a film inner direction, by physical vapor phase deposition.

SOLUTION: A thin film magnet includes a hard magnetic phase which contains a rare earth element, and a soft magnetic phase which contains Fe and/or Co. A hard magnetic phase constituting element and a soft magnetic phase constituting element are deposited on a board by using physical vapor phase deposition. As the physical vapor phase deposition, sputtering is preferable. At that time, the temperature of the board is preferably at 300-800°C The average crystal grain diameter of the soft magnetic phase is preferably 5-60 nm, and the average crystal grain diameter of the soft magnetic phase is preferably 5=50 nm. Furthermore, the axis of easy magnetization of the soft magnetic phase is preferably oriented. The thin film magnet has a coercive force of 3 kOe or more and a maximum energy product of 12 MGOe or more.

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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the thin film magnet applied to the motor of the minimum size etc., and its manufacture method.

[0002]

[Description of the Prior Art] Recently, the motor of very small size etc. is increasingly needed from a rise of the need of improvement in processing technology and the micro machine below milli size. In order to miniaturize a motor, thickness is thin and the magnet excellent in the performance per unit volume is needed.

[0003] As the production method of a thin magnet, the method of carrying out the grinding process of the sintered magnet, the method of carrying out strip processing of the flexible magnet with a roll etc., etc. are mentioned, for example. However, since problems, such as a fall of a mechanical strength, oxidization, and property degradation by processing distortion, arise when carrying out the grinding of the sintered magnet, it is difficult to consider as the thickness of about 300 micrometers or less. On the other hand, a flexible magnet is the composition which distributed magnet powder in rubber or the resin, and since the volume pulse duty factor of magnet powder is low, a high property is not acquired. When it thin-shape-izes, the fall of a magnet property is remarkable and stops therefore, being equal to practical use.

[0004] On the other hand, in JP,9-266113,A, it has proposed applying the exchange spring magnet with which the magnet property exceeding the conventional rare earth permanent magnet is acquired to a thin film magnet. Generally, the large elasticity magnetism phase of magnetization and a hard magnetism phase with large coercive force are joining together magnetically by the exchange interaction, and an exchange spring magnet is a magnet with which a high-energy product is obtained. In this official report, in order to thin-film-ize such an exchange spring magnet, it is considering as the composite construction to which the laminating of a hard magnetism layer with a thickness of 1-700nm and the soft-magnetism layer was carried out by the spatter, respectively, and switched connection of both was carried out. Thus, by making a thin film magnet into exchange spring structure, a magnet property can be made high compared with a thin film magnet, a thin shape flexible magnet, etc. by grinding of a sintered magnet. For example, in the example 2 of this official report, a hard magnetism layer is set to Sm (Co, Fe, Cu, Zr)<sub>7</sub>, and a soft-magnetism layer is made into Fe-Co. The magnet of coercive force  $iH_c=120 \text{ kA/m}$  (1.5kOe) and maximum energy product (BH)  $\text{max}=155 \text{ kJ/m}^3$  (19.5MGOe) is obtained. in the example 3 A hard magnetism layer is set to Sm<sub>2</sub>Fe<sub>17</sub>N<sub>3</sub>, and a soft-magnetism layer is set to Fe. Coercive force  $iH_c=530 \text{ kA/m}$  (6.6kOe), The magnet of maximum energy product (BH)  $\text{max}=250.7 \text{ kJ/m}^3$  (31.3MGOe) is obtained. in sample No.5 of an example 6 A hard magnetism layer is considered as Nd-Fe-Co-aluminum-Ga-B system composition, and it is a soft-magnetism layer. It considers as Fe-Co and the magnet of coercive force  $iH_c=1070.8 \text{ kA/m}$  (13.4kOe) and maximum energy product (BH)  $\text{max}=207.5 \text{ kJ/m}^3$  (25.9MGOe) is obtained. Moreover, if a spatter is used for manufacture of a thin film magnet in this way, since the unification with the equipment incorporating a magnet can be performed

without using technique, such as adhesion, the simplification of a process is possible.

[0005] However, by the method of realizing an exchange spring magnet by carrying out the laminating of a soft-magnetism layer and the hard magnetism layer by the sputter, since it is necessary to carry out the sputter of two or more targets by turns, the number of sheets of a target increases and there is a problem that a sputtering system will become expensive. Moreover, by this method, since it is difficult to control the structure of the interface of a soft-magnetism layer and a hard magnetism layer, it is stabilized and the problem of being difficult has also produced the highly efficient thin film magnet.

[0006] By the way, although the method of forming a rare earth alloy thin film magnet also in JP,4-99010,A by the sputter is indicated, there is no publication about an exchange spring magnet in this official report. The thin film magnet currently produced in the example of this official report is a rare earth alloy magnet of a Nd-Fe-B system and a Pr-Fe-B system. In this example, highest maximum energy product (BH) max is 14MGOe(s), and the rare-earth-elements (R) content at that time is 18 atom %. On the other hand, although the lowest value of R content is nine atom % in this example, (BH) max at this time is only 8MGOe(s). the rare earth alloy thin film magnet currently produced in the example of this official report since the content of R in the ratio of R occupied in  $R_2Fe_{14}B$ , i.e., a stoichiometric composition, is 11.76 atom % --  $R_2Fe_{14}B$  -- adding -- this -- R -- the time of a rich phase existing -- (BH) max -- high -- becoming -- this -- R -- when a PUA phase exists, it is thought that (BH) max becomes low since the elasticity magnetism phase which consists of an  $\alpha$ -Fe phase etc. besides  $R_2Fe_{14}B$  which is a hard magnetism phase exists comparatively so much, although composition of the whole magnet serves as R PUA with an exchange spring magnet compared with a stoichiometric composition -- the magnet property at that time -- R -- it becomes higher than the case of being rich. Therefore, it is clear the thin film magnet's currently produced in the example of this official report not to have exchange spring structure. In addition, although, as for the thin film magnet of 9 atom %, an  $\alpha$ -Fe phase may exist [ R content in the example of this official report ], in view of composition, it is thought of because one [ at least ] diameter of crystal grain of a hard magnetism phase and an elasticity magnetism phase is too large that it is not an exchange spring magnet.

[0007] By the method indicated by above-mentioned JP,4-99010,A, since it is not necessary to consider as a cascade screen, there is little number of sheets of a sputter target, it ends, and can use the thing of simple structure also for a sputtering system. However, since it is not an exchange spring magnet, in order to obtain high magnetic properties, R content will have to be made high, and raw material cost will become high. Moreover, compared with the thin film magnet of exchange spring structure, the magnet property expected theoretically is also a low.

[0008]

[Problem(s) to be Solved by the Invention] The purpose of this invention is cheap and is offering a thin film magnet with a high magnet property moreover.

[0009]

[Means for Solving the Problem] Such a purpose is attained by one composition of following the (1) - (14).

(1) The thin film magnet which the hard magnetism phase and elasticity magnetism phase which adjoin mutually in film surface inboard exist including the hard magnetism phase containing rare earth elements, and the elasticity magnetism phase containing Fe and/or Co, and is formed by the physical gaseous-phase depositing method.

(2) The thin film magnet of the above (1) whose diameter of average crystal grain of an elasticity magnetism phase the diameter of average crystal grain of a hard magnetism phase is 5-500nm, and is 5-60nm.

(3) The above (1) or (2) thin film magnets whose thickness is 0.01-300 micrometers.

(4) One thin film magnet of above-mentioned (1) - (3) in which the easy axis of a hard magnetism phase is carrying out orientation.

(5) One thin film magnet of above-mentioned (1) - (4) whose coercive force is 3 or more kOes.

(6) One thin film magnet of above-mentioned (1) - (5) whose maximum energy products are 12 or more MGOes.

- (7) One thin film magnet of above-mentioned (1) - (6) with which a hard magnetism phase contains R (R is at least one sort of the rare earth elements containing Y), T (T is Fe, or Fe and Co), and B, and an elasticity magnetism phase contains T.
- (8) One thin film magnet of above-mentioned (1) - (6) with which a hard magnetism phase contains R (R is one or more sorts of rare earth elements, and surely contains Sm), T (T is Fe, or Fe and Co), and N, and an elasticity magnetism phase contains T.
- (9) One thin film magnet of above-mentioned (1) - (6) with which a hard magnetism phase contains R (R is one or more sorts of rare earth elements), and Co, and an elasticity magnetism phase contains Co.
- (10) One thin film magnet of above-mentioned (1) - (9) which has a protective coat on a front face.
- (11) The above (1) The manufacture method of a thin film magnet of having the process which it is [ process ] the method of manufacturing one thin film magnet of - (10), and the physical gaseous-phase depositing method is used [ process ], and makes a hard magnetism phase composition element and an elasticity magnetism phase composition element depositing on a substrate simultaneously.
- (12) The manufacture method of the thin film magnet the above (11) that the aforementioned physical gaseous-phase depositing method is a spatter.
- (13) The manufacture method of the thin film magnet the above (12) which makes temperature of the substrate by which a thin film magnet is formed in a front face 300-800 degrees C in the aforementioned spatter.
- (14) The manufacture method of one thin film magnet of above-mentioned (11) - (13) which heat-treats at 300-800 degrees C after making a hard magnetism phase composition element and an elasticity magnetism phase composition element deposit on a substrate simultaneously.

[0010]

[Function and Effect] A hard magnetism thin film given [ aforementioned ] in JP,9-266113,A carries out the laminating of a hard magnetism layer and the soft-magnetism layer by turns by the spatter, and is taken as exchange spring structure. That is, a hard magnetism thin film given [ this ] in an official report serves as the structure where a hard magnetism phase and an elasticity magnetism phase adjoin only in a direction perpendicular to a film surface.

[0011] On the other hand, it faces manufacturing the thin film magnet of exchange spring structure, and a hard magnetism phase composition element and an elasticity magnetism phase composition element are made to deposit simultaneously on a substrate in this invention. The final organization of the thin film magnet obtained using this method becomes what the hard magnetism phase and the elasticity magnetism phase distributed to homogeneity mostly in the film. That is, the hard magnetism phase and elasticity magnetism phase which adjoin mutually in film surface inboard will exist. Since the property as an exchange spring magnet is discovered with such organization, although there is less amount of the rare earth elements used than a thin film magnet given [ above-mentioned ] in JP,4-99010,A, the magnet property more than equivalent is acquired.

[0012] Moreover, since it is not necessary to carry out a spatter by turns even when there are few targets and it ends with this invention, when using a spatter, for example, since it is not necessary to consider as a laminated structure which was indicated by aforementioned JP,9-266113,A, and using two or more targets, the composition of a sputtering system is simple, and ends and a manufacturing cost becomes low. Moreover, in this invention, in order to form the complex tissue which consists of a hard magnetism phase and an elasticity magnetism phase by heat treatment after spatter film formation, or substrate heating at the time of a spatter, the interface of a bi-phase becomes smooth. On the other hand, it is difficult to be stabilized and to obtain it, though a high magnet property is acquired by the method indicated by aforementioned JP,9-266113,A, i.e., the method of carrying out the laminating of the layer which consists of an elasticity magnetism phase, and the layer which consists of a hard magnetism phase by the spatter, since the conditions for forming the interface of a bi-phase smoothly are severe.

[0013]

[Embodiments of the Invention] The thin film magnet of a thin film magnet this invention is a rare earth exchange spring magnet containing the hard magnetism phase containing rare earth elements, and the elasticity magnetism phase containing Fe and/or Co.

[0014] In order to obtain high coercive force, 5-60nm of diameters of average crystal grain of an elasticity magnetism phase is more preferably set to 5-40nm. In a magnet, a hard magnetism phase with a high crystal magnetic anisotropy and an elasticity magnetism phase with high saturation magnetization exist, since the elasticity magnetism phase is detailed, the interface of a bi-phase increases, the effect of an exchange interaction becomes large, and it is thought that high coercive force is obtained. If the diameter of average crystal grain of an elasticity magnetism phase is too small, saturation magnetization will become low, and if too large, coercive force and square shape nature will become low.

[0015] The partial component analysis (transverse electromagnetic-EDX) by the transmission electron microscope can investigate the distinction with an elasticity magnetism phase and a hard magnetism phase, and composition of each phase. In addition, generally an elasticity magnetism phase is an indeterminate form.

[0016] The diameter of average crystal grain of an elasticity magnetism phase is computed by image analysis. First, the piece for measurement of a magnet is produced using etching etc., and a total of  $S$  is computed by the image analysis of severaln of crystal grain, and the cross section of each crystal grain about the elasticity magnetism phase contained all over the measuring object field. And average cross-section  $S/n$  per crystal grain of an elasticity magnetism phase is computed, and let diameter-of-circle  $D$  whose area is  $S/n$  be a diameter of average crystal grain. That is, the diameter  $D$  of average crystal grain is a formula. It asks from  $\pi(D/2)^2=S/n$ . In addition, as for a measuring object field, it is desirable to set up so that  $n$  may become 50 or more.

[0017] the rate of the elasticity magnetism phase in a thin film magnet -- desirable -- ten to 90 volume % -- it is ten to 80 volume % more preferably Even if the rate of an elasticity magnetism phase is too low and it is too high, a good magnet property becomes is hard to be acquired, and especially a maximum energy product tends to become low. The rate of an elasticity magnetism phase is searched for by the so-called areal analysis using the transmission-electron-microscope photograph of a magnet cross section. In this case, an area ratio turns into a volume ratio.

[0018] 5-500nm of diameters of average crystal grain of a hard magnetism phase is 5-100nm more preferably. When the diameter of average crystal grain of a hard magnetism phase is too small, crystallinity is inadequate, and high coercive force is hard to be obtained. On the other hand, since an exchange interaction will become small when the area of an interface with an elasticity magnetism phase decreases if the diameter of average crystal grain of a hard magnetism phase is too large, a residual magnetic flux density becomes small, and a remanence ratio ( $H_k/H_cJ$ ) becomes low. Moreover, if the diameter of average crystal grain of a hard magnetism phase is too large, in applying this invention to the rare earth nitriding magnet mentioned later, the problem that the time which nitriding treatment takes becomes long arises. The diameter of average crystal grain of a hard magnetism phase is computed like the diameter of average crystal grain of an elasticity magnetism phase.

[0019] In addition, Above  $H_k$  is external-magnetic-field intensity in case flux density turns into 90% of a residual magnetic flux density in the 2nd quadrant of the magnetic hysteresis loop. A maximum energy product with as high  $H_k$  as a low is not obtained.  $H_k/H_cJ$  serves as an index of a magnet performance and expresses the square degree in the 2nd quadrant of the magnetic hysteresis loop. Since the distribution of the micro coercive force in a magnet becomes sharp so that  $H_k/H_cJ$  is large, even if the peculiar coercive force  $H_cJ$  is equivalent, magnetizing becomes easy, magnetization dispersion also decreases, and a maximum energy product becomes high. And the stability of the magnetization to change of the demagnetizing field from the outside at the time of magnet use or self-demagnetizing field becomes good, and it becomes that by which the performance of the magnetic circuit containing a magnet was stabilized.

[0020] As for a hard magnetism phase, it is desirable that it is that in which the easy axis is carrying out orientation.

[0021] In addition to the above-mentioned hard magnetism phase and the above-mentioned elasticity magnetism phase, other phases may be contained in the magnet. However, as for the ratio without magnetism of an unusual appearance, it is desirable that it is below 5 volume % of the whole magnet.

[0022] 300 micrometers or less of magnetic thickness are more preferably set to 100 micrometers or

less. If a magnet is too thick, the miniaturization of the device to apply will become difficult. There is especially no minimum of magnet thickness, and although what is necessary is just to secure the thickness which is the grade from which the function as an exchange spring magnet is not prevented, it usually considers as the thickness of 0.01 micrometers or more.

[0023] Especially the configuration of a thin film magnet may not be limited, but cross sections may be any, such as the shape of a straight line, an arc-shaped plate, and tube-like objects, such as a cylinder. In addition, a tubed thin film magnet can be formed by performing a spatter and vacuum evaporation, rotating pillar-shaped objects, such as the shape of a pillar.

[0024] The coercive force of 3 or more kOes and the maximum energy product of 12 or more MGOes can be obtained by choosing suitable composition and controlling organization by the thin film magnet of this invention as mentioned above. Moreover, it is also possible by anisotropy-izing magnetically to acquire a still higher magnet property.

[0025] Next, composition of the thin film magnet of this invention is explained.

[0026] In the thin film magnet of this invention, although especially each composition of a hard magnetism phase and an elasticity magnetism phase is not limited, as for an elasticity magnetism phase, it is usually desirable that it is desirable R and Co (R is rare earth elements), or that a hard magnetism phase makes R and Fe a principal component at least at least, and it makes a principal component alpha-Fe, Fe-Co, Fe-B, or Fe-N.

[0027] What is explained below, for example is mentioned as a combination with both the desirable magnetism phase.

[0028] (1) The thin film magnet of thin film \*\*\*\*\* with which a hard magnetism phase contains R (R is at least one sort of the rare earth elements containing Y), T (T is Fe, or Fe and Co), and B, and an elasticity magnetism phase contains T is an exchange spring magnet of an R2T14B system. since a sintering reaction advances by R rich phase's turning into the liquid phase, and flowing in an R2T14B system sintered magnet -- whole composition -- general -- R2T14B -- R, although it becomes rich With the thin film magnet of this invention, since a hard magnetism phase consists of R2T14B substantially and an elasticity magnetism phase consists of T substantially, whole composition serves as R PUA from R2T14B.

[0029] The desirable contents of each element in this thin film magnet are R:4 to 10 atom %, and B:5 to 25 atom %, and the remainder is T substantially.

[0030] Although at least one sort, especially Nd are desirable and it is desirable as R that Dy is included further among Nd, Pr, and Tb, in addition to these, one or more sorts in La, Ce, Gd, Er, Ho, Eu, Pm, Tm, Yb, and Y may also be included. Mixture, such as a misch metal, can also be used as a raw material of rare earth elements. If there are too few R contents, a hard magnetism phase will decrease and high coercive force will become is hard to be obtained. On the other hand, if there are too many R contents, a high residual magnetic flux density will become is hard to be obtained, and also a cost rise is caused.

[0031] As for the amount of Co(es) in T, it is desirable to carry out to below 30 atom %.

[0032] If there are too few B contents, high coercive force will no longer be obtained, and if there are too many B contents, a high residual magnetic flux density will no longer be obtained.

[0033] Although Element MI (MI is one or more sorts of aluminum, Cr, Mn, Mg, Si, Cu, C, Nb, Sn, W, V, Zr, Ti, Mo, and Ga) may be added in order to improve coercive force, if the addition of Element MI exceeds 10 atom %, the fall of magnetization will pose a problem.

[0034] In addition, an elasticity magnetism phase is a T phase of bcc structure. Specifically, it is thought that it is an alpha-Fe phase substantially, or it is Fe-B system compounds, such as that by which a part of Fe of an alpha-Fe phase was replaced by Co, B, R, etc., for example, Fe3B, and Fe2B, etc., or they are these mixed phases.

[0035] (2) The thin film magnet of thin film \*\*\*\*\* with which a hard magnetism phase contains R (R is one or more sorts of rare earth elements, and surely contains Sm), T (T is Fe, or Fe and Co), and N, and an elasticity magnetism phase contains T is a rare earth nitriding magnet. To this thin film magnet, it is desirable to contain further Element MII (for MII(s) to be at least one sort of elements chosen from Zr, Ti, V, Cr, Nb, Hf, Ta, Mo, W, aluminum, C, P, and Ga) besides R, T, and N.



[0036] A hard magnetism phase is the structure with which R, T, and N were made into the subject, it had TbCu<sub>7</sub> type crystal structure of hexagonal system, and/or the Th<sub>2</sub>Zn<sub>17</sub> type crystal structure, and nitrogen invaded into these crystal structures. In the TbCu<sub>7</sub> type crystal structure, R exists in Tb site and T exists mainly in Cu site. Although MII changes also with elements, it may exist mainly in Tb site and may exist in Cu site. Moreover, although MII may dissolve to the bcc structure T phase which is an elasticity magnetism phase, it may form another compound by MII and T. In the Th<sub>2</sub>Zn<sub>17</sub> type crystal structure, R exists in Th site and T exists mainly in Zn site. It is thought that the site which MII replaces changes with kinds of MII.

[0037] An elasticity magnetism phase is a T phase containing T phase of bcc structure, and/or N. It is thought that it is an alpha-Fe phase substantially, or a part of Fe of an alpha-Fe phase is replaced by Co, MII, R, etc., or bcc structure T phases are these mixed phases. Moreover, it is thought that T phase containing N consists of the solid solution of nitrogen, a nitride of T, etc.

[0038] In addition, in a magnet, a Fe<sub>3</sub>Zr phase etc. may be contained as crystal phases other than the above-mentioned hard magnetism phase and an elasticity magnetism phase.

[0039] the content of R -- desirable -- four to 9 atom % -- it is five to 7.5 atom % more preferably the content of N -- desirable -- ten to 20 atom % -- more -- desirable -- 12 to 18 atom % -- further -- desirable -- 13 to 18 atom % -- it is 13.5 to 18 atom % most preferably the content of MII -- desirable -- one to 10 atom % -- it is 2.5 to 5 atom % more preferably And the remainder is T substantially.

[0040] Coercive force will become low if there are too few contents of R. Since the amount of a bcc structure T phase will decrease, and a magnet property will become low and expensive R will be used so much on the other hand when there are too many contents of R, a cheap magnet is no longer obtained. As R other than Sm, it is desirable to use one or more sorts, such as Y, La, Ce, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. A hard magnetism phase is the composition that nitrogen invaded into the crystal structure of TbCu<sub>7</sub> type or Th<sub>2</sub>Zn<sub>17</sub> type, and with such a hard magnetism phase, when R is Sm, it shows the highest crystal magnetic anisotropy. Since a crystal magnetic anisotropy will fall and coercive force will also decline if the ratio of Sm is low, Sm ratio in R is more preferably carried out to more than 70 atom % more than 50 atom %.

[0041] If there are too few N contents, it will become inadequate the rise of Curie temperature, improvement in coercive force, improvement in a remanence ratio, the improvement in saturation magnetization, and a maximum energy product's improving, when there are too many N contents, while the inclination for a residual magnetic flux density to fall is shown, a remanence ratio becomes low and a maximum energy product also becomes low. N content can be measured by the gas-analysis method etc.

[0042] If Element MII is not contained, crystal grain with a big and rough elasticity magnetism phase becomes easy to deposit at the time of heat treatment for the time of membrane formation, or crystallization. Although what is necessary is just to heat-treat on suitable conditions in order to make this into homogeneous and detailed organization, since the width of face of the conditions permitted at this time is narrow, as for Element MII, containing fundamentally is desirable. Moreover, coercive force also improves by adding Element MII. However, if there are too many contents of MII, a residual magnetic flux density will become low.

[0043] The remainder except each above-mentioned element is T substantially. T is whether it is Fe, and Fe and Co. Although addition of Co raises a property, as for the ratio of Co in T, it is desirable that it is below 50 atom %. If the ratio of Co exceeds 50 atom %, a residual magnetic flux density will become low.

[0044] (3) The desirable composition in the thin film magnet of thin film \*\*\*\*\* with which a hard magnetism phase contains R (R is one or more sorts of rare earth elements) and Co, and an elasticity magnetism phase contains Co is R:6 to 15 atom %, and the remainder is Co substantially. In addition, although a part of Co may be replaced by other transition elements, such as Fe and Cu, in order to suppress the fall of magnetic properties, it is desirable to make the substitutional rate of Co by these elements below into 50 atom %.

[0045] As R, one or more sorts, such as Sm, Y, La, Ce, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu,



are desirable, and it is more desirable that Sm is contained at least.

[0046] Hard magnetism phases are  $R_2Co_{17}$  and a mixed phase which consists of  $RCo_7$  or  $RCo_5$ , or contains these at least two sorts substantially, and an elasticity magnetism phase consists of  $Co(es)$  substantially. In addition, a part of Co may be replaced in each phase by other elements which were described above.

[0047] In addition, in the thin film magnet shown in above-mentioned (1) - (3), oxygen, carbon, hydrogen, etc. may be contained as an others and minute amount additive or an unescapable impurity. [ element / each / above-mentioned ]

[0048] Since a protective coat rare earth permanent magnet tends to oxidize, it is desirable to prepare a protective coat in the front face of a thin film magnet.

[0049] What is necessary is not to limit especially the composition of a protective coat, but to choose suitable composition according to magnet composition, and just to determine thickness that sufficient protective effect is obtained. Transition-metals oxide films, such as transition-metals nitride films, such as the film; inorganic compound film which consists of a metal membrane, for example, Ti, Ta, Cr, Mo, nickel, etc., as an example of a protective coat, for example, TiN, FeN, CrN, etc., and NiO, FeO; the resin film which consists of an organic compound film, for example, an epoxy resin, phenol resin, polyurethane, polyester, etc. is mentioned. When it constitutes a protective coat from a metal or an inorganic compound, as for thickness, it is desirable to be referred to as about 0.01-10 micrometers, and when it constitutes a protective coat from an organic compound, as for thickness, it is desirable to be referred to as 3-10 micrometers.

[0050] The thin film magnet of a substrate this invention is formed on a substrate using the physical gaseous-phase depositing methods, such as a spatter, so that it may mention later. As a substrate, you may use any, such as non-magnetic material, such as glass and nonmagnetic ceramics, and the magnetic substance, such as Fe. For example, it is also possible to use as a substrate the yoke which constitutes a magnetic circuit.

[0051] Between a ground layer thin film magnet and a substrate, you may prepare a ground layer if needed. By preparing the suitable ground layer according to magnet composition, it is possible to promote magnetic anisotropy-ization of the thin film magnet by substrate heating at the time of the spatter mentioned later. As a ground lamination element, Ti, Mo, Cr, Ta, Si, W, etc. are desirable, and should just choose suitably in consideration of matching of a lattice constant etc. according to composition of a thin film magnet, for example. As for ground layer thickness, it is desirable to be referred to as about 10-100nm.

[0052] The manufacture method, next the manufacture method of the thin film magnet of this invention are explained.

[0053] It faces manufacturing the thin film magnet of this invention, the physical gaseous-phase depositing method is used, and a hard magnetism phase composition element and an elasticity magnetism phase composition element are made to deposit on a substrate simultaneously.

[0054] As a physical gaseous-phase depositing method, a spatter, a vacuum deposition, or the ion plating method is desirable, and a spatter is desirable especially.

[0055] Especially the conditions in a spatter are not limited but should just perform a spatter using two or more targets containing at least one sort of these elements, using the target which contains a hard magnetism phase composition element and an elasticity magnetism phase composition element in rare-gas atmosphere, such as Ar. In addition, usually, although it is also possible to introduce nitrogen, to perform a reactant spatter and to form a nitride thin film directly into spatter atmosphere in case the thin film magnet containing R, T, and N which were mentioned above is manufactured, after forming an alloy thin film by the spatter, it considers as the composition which performs nitriding treatment mentioned later.

[0056] Although especially the substrate temperature in a spatter is not limited, it is possible by controlling substrate temperature to control the crystallinity of a thin film magnet and crystal orientation. For example, since the thin film of the shape of amorphous [ almost homogeneous ] is obtained when substrate temperature is carried out near a room temperature, although heat treatment for crystallization

and phase separation is indispensable, when substrate heating is performed, the thin film which the hard magnetism phase and the elasticity magnetism phase separated can be formed. For crystallization, 300 degrees C or more of substrate temperature are more preferably made into 400 degrees C or more. However, if substrate temperature is too high, since high coercive force will become are hard coming to work an exchange interaction by growth of a crystal phase, and is hard to be obtained, 800 degrees C or less of substrate temperature are more preferably made into 750 degrees C or less. Moreover, it is also possible by controlling substrate temperature to such within the limits to carry out orientation of the easy axis of a hard magnetism phase.

[0057] As for the method of carrying out orientation of the easy axis of a hard magnetism phase by substrate heating, it is desirable to apply to the R2T14B system composition and R-T-N system composition which were mentioned above. Although the direction of orientation in this method changes with magnet composition and is influenced of orientation conditions (the kind of ground layer, substrate temperature, etc.), it usually becomes almost perpendicular to a thin film magnet principal plane by R2T14B system composition, and turns into field inboard of a thin film magnet in R-T-N system composition.

[0058] Moreover, it is desirable to carry out orientation of the easy axis in the R-Co system composition mentioned above not by substrate heating but by magnetic field impression for orientation at the time of membrane formation. The direction of orientation in this case usually turns into the direction of the impressed magnetic field.

[0059] After forming an amorphous-like thin film, it heat-treats for crystallization. Although what is necessary is just to determine the conditions of this heat treatment suitably according to composition so that the desired crystalline structure may be obtained, usually, processing temperature is desirable, and they are more preferably made into 400-750 degrees C 300-800 degrees C, and make the processing time 0.05 - 5 hours more preferably for 0.01 to 10 hours. It is desirable to perform heat treatment in inert gas atmosphere, such as Ar and helium, and a vacuum, in order to prevent oxidization of a thin film. With this heat treatment, the phase which turns into a hard magnetism phase by the hard magnetism phase or nitriding, and an elasticity magnetism phase deposit. If heat treatment temperature is too low, crystallization and phase separation will tend to become inadequate. On the other hand, if heat treatment temperature is too high, an elasticity magnetism phase will grow too much, and coercive force will become easy to decline, and it will become easy to produce an unusual appearance depending on composition.

[0060] In addition, even when the thin film formed by the spatter is crystallizing, you may heat-treat if needed. For example, it is possible by heat-treating to cut down or eliminate an unusual appearance. What is necessary is just to perform heat treatment for such crystalline-structure control on the same conditions as heat treatment for the above-mentioned crystallization.

[0061] In producing the thin film magnet containing R, T, and N which were mentioned above, it usually performs nitriding treatment after heat treatment for crystallization. In addition, in performing heat treatment for crystalline-structure control, it performs nitriding treatment after this heat treatment. Nitriding treatment is performed by heat-treating to a thin film in nitrogen-gas-atmosphere mind. Of this nitriding treatment, a nitrogen atom invades into crystal phases, such as TbCu7 type crystal, the invaded type solid solution is formed, and it becomes a hard magnetism phase by it. 350-700 degrees C of processing temperature in the case of nitriding treatment are 350-600 degrees C more preferably, and the processing time is 0.1 - 300 hours preferably. As for the pressure of nitrogen gas, it is desirable to consider as about 0.1 or more atmospheric pressure. In addition, high-pressure nitrogen gas can be used for nitriding treatment, nitrogen gas + hydrogen gas can be used, or ammonia gas can also be used.

[0062] Especially the use of the thin film magnet of a use this invention is not limited, but can be applied to the various devices by which a miniaturization is demanded. For example, it is suitable for the magnet for bias magnetic field impression of the stator of a micro motor, and a permanent magnet bias type MR head (magnetoresistance-effect type head), a small actuator, a magnetometric sensor, etc. That to which orientation of the easy axis was carried out at right angles to a film surface when applying to the stator of a motor is desirable, and when applying to the thin film for bias magnetic field impression,

what carried out orientation of the easy axis to membranous field inboard is desirable.

[0063]

[Example] The thin film magnet sample shown in the example 1 following table 1 was produced using the RF magnetron-sputtering method. First, after having decompressed the inside of a vacuum tub to  $6 \times 10^{-6}$  or less Torr, next performing the pre sputter for 15 minutes and removing the oxide on the front face of a target, the alloy thin film was formed. In addition, the target was manufactured by carrying out a hotpress, after grinding the alloy ingot manufactured by the arc dissolution. Glass was used for the substrate. Heating of a substrate was not performed. Sputter atmosphere was made into Ar gas of 5mTorr(s), and injection power was set to 250W.

[0064] Thus, the obtained alloy thin film was 1 micrometer in thickness, and was in the amorphous state altogether.

[0065] Next, it heat-treated to each alloy thin film for crystallization, and considered as the thin film magnet sample at it. Conditions when the optimum conditions of heat treatment, i.e., the highest maximum energy product, are acquired are shown in Table 1. Composition (whole composition) of each sample is shown in Table 1. ICP investigated composition.

[0066] The residual magnetization ( $\sigma_r$ ) of these samples, coercive force ( $H_cJ$ ), and the maximum energy product  $[(BH)_{max}]$  were measured by VSM. The measurement direction was made into the direction parallel to a film surface. A result is shown in Table 1. In addition, the magnetic properties shown in Table 1 are the things at the time of heat-treating by optimum conditions.

[0067] When X-ray (Cu-K alpha rays) diffraction and transverse electromagnetic-EDS investigated each sample, it is the polycrystal complex tissue containing a hard magnetism phase (Nd<sub>2</sub>Fe<sub>14</sub>B type crystal phase) and an elasticity magnetism phase (bcc structure alpha-Fe phase), and the amorphous phase had disappeared substantially. The rate of an abundance ratio of the elasticity magnetism phase in the diameter of average crystal grain of the elasticity magnetism phase for which it asked by transverse electromagnetic-EDX, and a sample is shown in Table 1. In addition, the diameter of average crystal grain of the hard magnetism phase of each sample suited the range of 20-50nm.

[0068]

[Table 1]

表 1

サンプル No.	磁石組成 (原子%)					$\sigma_r$ (emu/g)	$H_cJ$ (kOe)	$(BH)_{max}$ (MGOe)	軟質磁性相		熱処理 条件
	Nd	B	M'	Fe	Co				結晶粒径 (nm)	比率 (体積%)	
101	4.5	20.5	Si:1.0	残部	—	123.6	3.1	13.2	20~40	70	650°C、10min.
102	4.0	20.4	Ga:1.0	残部	—	124.1	3.8	14.0	20~40	80	650°C、10min.
103	5.0	20.8	Cr:5.0	残部	8.0	111.6	4.5	13.0	25~45	50	670°C、10min.
104	9.1	6.0	V:1.0	残部	8.0	121.1	5.4	17.6	20~40	25	650°C、10min.
105	9.5	6.0	V:1.0	残部	5.0	120.0	6.1	18.5	20~40	20	650°C、10min.

[0069] Table 1 shows that the exchange spring magnet of a high property is realized in the sputter film of a monolayer.

[0070] The thin film magnet sample shown in the example 2 following table 2 was produced.

[0071] First, composition of a target was changed and also the alloy thin film was formed on an example 1 and these conditions. The obtained alloy thin film was 1 micrometer in thickness, and was in the amorphous state altogether.

[0072] Next, it heat-treated to each alloy thin film for crystallization. Heat treatment conditions are shown in Table 2. This heat treatment condition is optimum conditions like Table 1.

[0073] Next, nitriding treatment was performed to each thin film, and it considered as the thin film magnet sample. Nitriding treatment was performed by heating at 400 degrees C in nitrogen-gas-

atmosphere mind for 10 hours. Composition of each sample is shown in Table 2. ICP investigated composition. However, the amount of N was calculated by gas analysis.

[0074] When X-ray (Cu-K alpha rays) diffraction and transverse electromagnetic-EDS investigated each sample, it is the polycrystal complex tissue containing a hard magnetism phase (a TbCu7 type crystal phase or Th2Zn17 type crystal phase) and an elasticity magnetism phase (bcc structure alpha-Fe phase), and the amorphous phase had disappeared substantially. In addition, it was only sample No.206 that the hard magnetism phase was a Th2Zn17 type crystal phase. The rate of an abundance ratio of the elasticity magnetism phase in the diameter of average crystal grain of the elasticity magnetism phase for which it asked by transverse electromagnetic-EDX, and a sample is shown in Table 2. In addition, the diameter of average crystal grain of the hard magnetism phase of each sample suited the range of 20-50nm.

[0075] The magnetic properties of these samples were measured like the example 1. A result is shown in Table 2. In addition, the magnetic properties shown in Table 2 are the things at the time of heat-treating by optimum conditions.

[0076]

[Table 2]

表 2

サンプル No.	磁石組成 (原子%)					$\sigma_r$ (emu/g)	HcJ (kOe)	(BH)max (MGOe)	軟質磁性相		熱処理 条件
	Sm	M <sup>II</sup>	N	Fe	Co				結晶粒径 (nm)	比率 (体積%)	
201	7.0	Zr:3.0	16	残部	4.0	102.3	8.8	16.5	20~40	15	700℃、0.5h
202	6.7	Zr:3.0	15	残部	—	100.2	8.5	15.8	30~50	20	700℃、0.5h
203	7.0	Zr:3.0 Ga:0.5	15	残部	4.0	101.5	10.0	16.8	20~40	17	700℃、0.5h
204	6.0	Zr:3.0	14	残部	4.0	106.4	7.2	14.2	30~50	30	700℃、0.5h
205	7.5	Zr:3.0	17	残部	4.0	98.4	10.2	15.0	20~40	10	700℃、0.5h
206	8.0	—	13	残部	—	113.7	3.2	14.0	30~50	25	650℃、0.5h

[0077] Table 2 shows that the exchange spring magnet of a high property is realized in the spatter film of a monolayer also in this composition system.

[0078] The thin film magnet sample shown in the example 3 following table 3 was produced.

[0079] First, composition of a target was changed and also the alloy thin film was formed on an example 1 and these conditions. The obtained alloy thin film was 1 micrometer in thickness, and was in the amorphous state altogether.

[0080] Next, it heat-treated to each alloy thin film for crystallization, and considered as the thin film magnet sample at it. Heat treatment conditions are shown in Table 3. This heat treatment condition is optimum conditions like Table 1. Composition of each sample is shown in Table 3. ICP investigated composition.

[0081] When X-ray (Cu-K alpha rays) diffraction and transverse electromagnetic-EDS investigated each sample, it is the polycrystal complex tissue containing a hard magnetism phase (an Sm2Co17 type crystal phase and/or SmCo7 type crystal phase) and an elasticity magnetism phase (Fe phase, Co phase, Fe-Co phase), and the amorphous phase had disappeared substantially. The rate of an abundance ratio of the elasticity magnetism phase in the diameter of average crystal grain of the elasticity magnetism phase for which it asked by transverse electromagnetic-EDX, and a sample is shown in Table 3. In addition, the diameter of average crystal grain of the hard magnetism phase of each sample suited the range of 20-60nm.

[0082] The magnetic properties of these samples were measured like the example 1. A result is shown in Table 3. In addition, the magnetic properties shown in Table 3 are the things at the time of heat-treating by optimum conditions.

[0083]

[Table 3]

表 3

サンプル No.	磁石組成 (原子%)				$\sigma_r$ (emu/g)	HcJ (kOe)	(BH)max (MGOe)	軟質磁性相		熱処理 条件
	Sm	Cu	Co	Fe				結晶粒径 (nm)	比率 (体積%)	
301	10.0	10.0	残部	10.0	97.4	6.0	15.0	20~40	35	600°C、10min.
302	11.0	—	残部	40.0	105.0	4.5	13.5	30~50	30	600°C、10min.
303	10.0	—	残部	—	85.2	8.0	14.0	20~40	35	750°C、10min.

[0084] Table 3 shows that the exchange spring magnet of a high property is realized in the spatter film of a monolayer also in this composition system.

[0085] In addition, when the substrate was heated at 550 degrees C on the occasion of a spatter and also the thin film magnet sample was produced like the above-mentioned example 1 and the example 2, the orientation of the easy axis of a hard magnetism phase was accepted. The direction of orientation was a direction perpendicular to a film surface with the sample of composition of an example 1, and was membranous field inboard with the sample of composition of an example 2. Moreover, when the magnetic field of 3kOe(s) was impressed to the field inboard of a substrate on the occasion of a spatter and also the thin film magnet sample was produced like the above-mentioned example 3, the orientation of an easy axis was accepted in field inboard.

[0086] From the above example to a book

[Translation done.]